

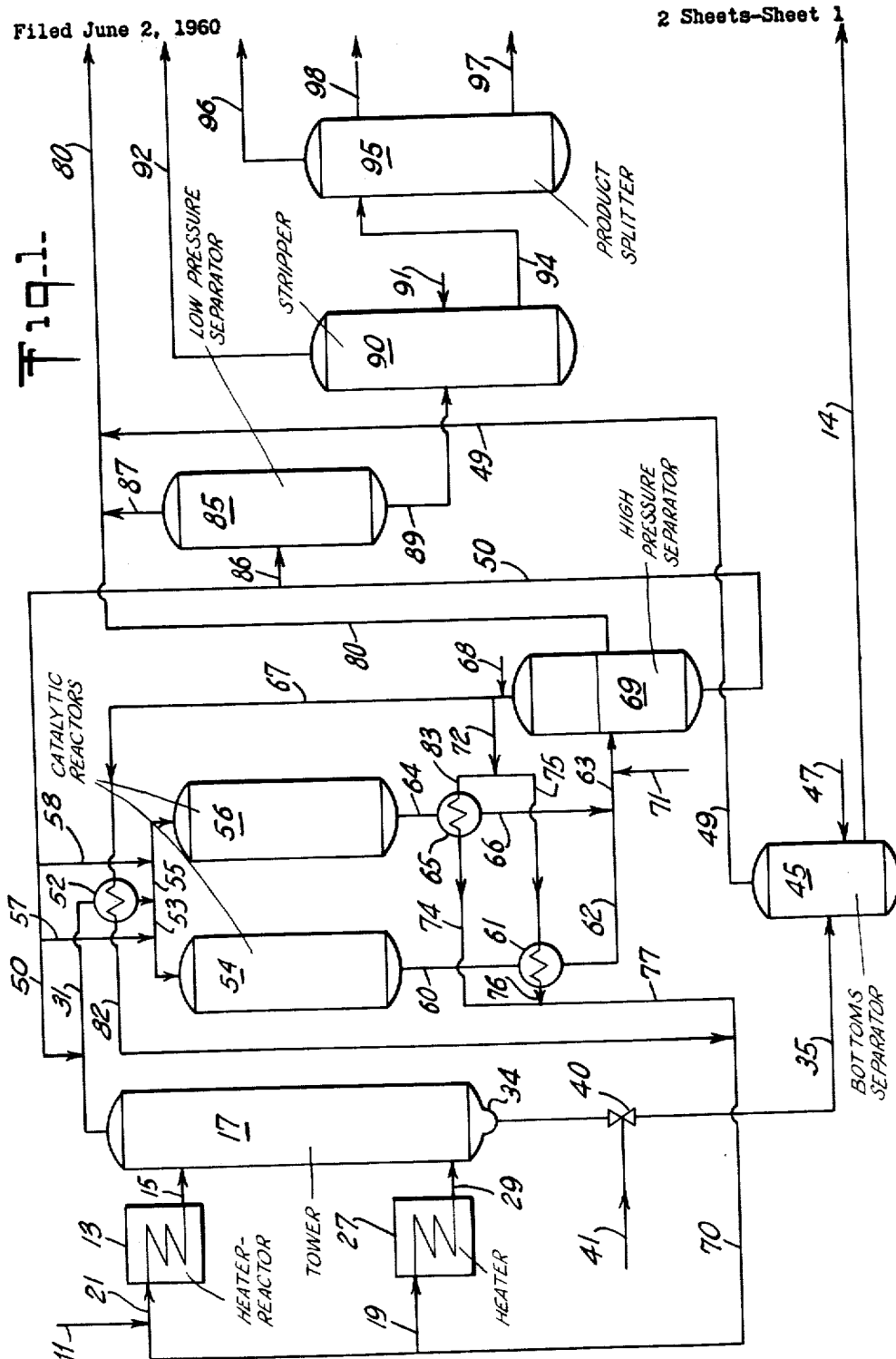
**May 14, 1963**

**DU BOIS EASTMAN ET AL**  
**HYDROCONVERSION OF HYDROCARBONS**

**3,089,843**

Filed June 2, 1960

2 Sheets-Sheet 1



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Fig. 3-

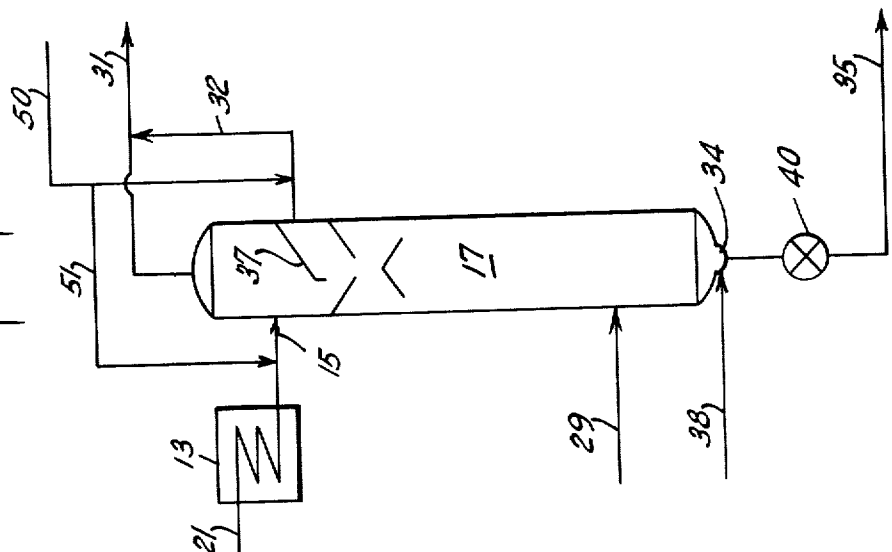
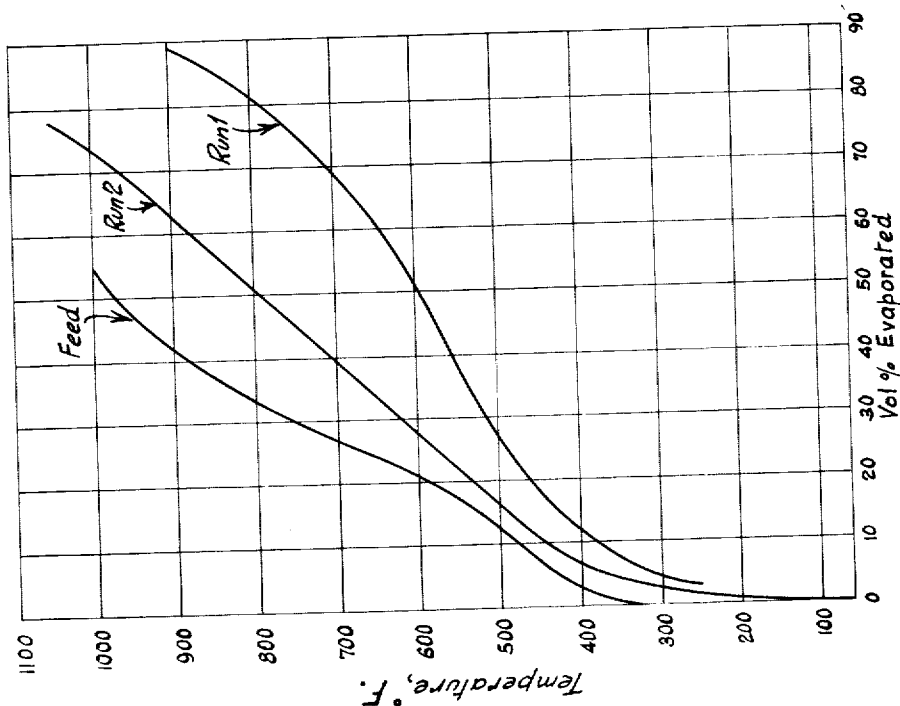


Fig. 2-



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3,089,843

## HYDROCONVERSION OF HYDROCARBONS

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Filed June 2, 1960, Ser. No. 33,582

26 Claims. (Cl. 208—58)

This invention relates to the treatment of hydrocarbon oils. More particularly, it is concerned with the conversion of crude oils or hydrocarbon oils containing heavy asphaltic and/or viscous materials into distillate products substantially free from sulfur, nitrogen, metals and ash- and gum-forming constituents.

In one aspect of the present invention a crude oil containing residual constituents is converted into a stable metal-free fraction containing components boiling in the middle distillate range in a yield considerably greater than is obtainable by conventional atmospheric and/or vacuum distillation. In another aspect of the invention a crude oil containing residual components is converted in an integrated operation into a stable substantially sulfur and nitrogen free distillate and which is also free from ash- and gum-forming constituents.

The process of the present invention employs relatively cheap hydrogen in amounts far in excess of the amounts actually consumed in the process. By the use of these large amounts of hydrogen, a heavy oil containing residual components such as whole crude or a reduced crude or the like is converted under controlled conditions to high yields of middle distillate without any substantial change in the naphtha content of the feed and without any substantial production of fixed hydrocarbon gases or heavy polymers or coke.

In the accompanying drawings FIG. 1 represents diagrammatically a flow scheme for the practice of the present invention. FIG. 2 shows graphically the high yields of middle distillate obtainable by the process of the present invention. FIG. 3 represents diagrammatically various modifications of the flow scheme of FIG. 1.

Referring now to FIG. 1, charge oil (as described below) from line 11 is mixed with a large excess of hydrogen in line 21 under elevated pressure and the mixture is introduced into heater 13 wherein it is passed through a coil heated indirectly as by oil or gas combustion. The hydrogen is mixed with the oil in an amount ranging from 5,000 to 95,000 standard cu. ft./bbl. of liquid feed, preferably from about 7,000 to about 30,000 standard cu. ft./bbl. of oil. Reaction temperatures within the coil are maintained between about 700 and 950° F., preferably between about 850 and 900° F. The heating coil outlet pressure is advantageously maintained within the range of 1,400 to 2,000 p.s.i.g., although pressures ranging from as low as 1,000 p.s.i.g. to as high as 5,000 p.s.i.g. may be employed.

The flow rate is such as to keep the reactant mixture in a state of extreme turbulence. In this state, the higher boiling hydrocarbons, under the conditions of temperature, hydrogen to oil ratio, contact time and pressure, are subjected to viscosity breaking with substantially immediate hydrogenation of the molecular fragments and without further breakdown, thereby materially increasing the production of middle distillates boiling in the 400–700° F. range without substantial increase in lower boiling gasoline range materials and without substantial formation of normally gaseous hydrocarbons and heavy tars and coke. As the reaction proceeds, the molecular fragments, because of their lower boiling characteristics, are substantially immediately vaporized.

The hot mixture of hydrogen, vaporized hydrocarbons

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and liquid oil leaves heater 13 by means of line 15 and is introduced substantially immediately into the upper section of tower 17. This section serves as a disengaging zone to separate gasiform materials comprising vaporous hydrocarbons and hydrogen from the liquid oil. The gasiform materials leave tower 17 through line 31 and the disengaged liquid flows downwardly through tower 17.

A separate hydrogen stream amounting to between 5,000 and 95,000 standard cubic feet per barrel of oil fed to heater 13, and preferably between about 10,000 and 80,000 cubic feet per barrel, is passed through line 19 to heater 27 wherein the hydrogen is heated indirectly as by oil or gas combustion to an elevated temperature between 800 and 900° F., preferably between about 825 and 880° F., while maintaining the outlet pressure of heater 27 substantially the same as the outlet pressure of heater 13. The hot hydrogen passes continuously from heater 27 through line 29 to the lower section of tower 17 at a point spaced above the bottom of the tower. The pressure within tower 17 is maintained at approximately the pressure of lines 15 and 29, advantageously within the range of 1400 to 2000 pounds per square inch. The disengaged liquid oil which has been separated from the vaporous hydrocarbons and hydrogen in the upper section of tower 17 flows downwardly and during its passage to the bottom of the tower is brought into intimate contact with the separately heated stream of hydrogen entering the lower part of tower 17 through line 29. Under the existing conditions of temperature, pressure and ratio of hydrogen to oil some further cracking and viscosity breaking takes place with hydrogenation of the unsaturated fragments, although the main action in the tower is a stripping of the lighter components from oil by the large quantity of hydrogen, the combined effect being the production of additional oil vapors and the reduction of the liquid oil to a heavy residuum containing substantially all of the metal and ash-forming constituents of the original charge oil. The vaporized portion of the downward flowing oil is swept upwardly by the unreacted hydrogen and passes through the tower and out of the upper portion thereof through line 31 with the vaporous hydrocarbons and hydrogen separated from liquid phase oil in the disengaging zone.

The remaining liquid hydrocarbons which contain substantially all of the metal contaminants present in the original hydrocarbon charge stock flow downwardly through tower 17 below the point of entry of line 29 and collect as a residual liquid fraction in boot 34 from which it may be withdrawn continuously or intermittently.

The yield of oil collected in boot 34 may be controlled as desired depending on the character of the oil charged to heater 13 by varying the charge rate, the temperature and/or pressure in the heating coil, the temperature within the tower and the relative quantity of hydrogen introduced through lines 15 and 29. The highest yield of treated vaporized oil which passes overhead through line 31 and the lowest yield of unvaporized oil collected in boot 34 is obtained by operating at increased temperature and time of reaction and increased quantity of hydrogen charged. In general, it is most desirable from an economic standpoint to carry out the operation under conditions to produce the lowest yield of residual oil while conducting the operation at such a level of severity of treatment as to avoid producing carbon deposition within the apparatus or an appreciable quantity of fixed hydrocarbon gases. When the charge stock is a relatively light material such as, for example, a typical Arabian crude, the yield of liquid bottoms amounts to about 5–15%, usually 5–10%, of the charge whereas when the charge stock is a very heavy material such as, for example, San Ardo crude or a blend of the same with a deasphalted residuum, the yield of

liquid bottoms amounts to about 15–25%, usually 15–20%, of the charge.

The bottoms are withdrawn through line 35 and while passing through pressure level control valve 40 are cooled by the introduction of cutter oil through line 41. Alternatively, the cutter oil may also be introduced into line 35 either upstream or downstream from valve 40. The cutter oil is advantageously a light petroleum oil as, for example, a light cycle gas oil. The mixture of tower bottoms and cutter oil which is now at a temperature between about 500 and 600° F. is then introduced into bottoms separator 45 where small amounts of entrained or dissolved gaseous or vaporous materials are separated from the liquid oil at a pressure between about 125 and 150 p.s.i.g. If desired the separation may be expedited by the introduction of pressurized steam through line 47. The separator bottoms are removed through line 14 and may be sent to storage or may be subjected to further treatment. Alternatively, the separator bottoms may be used directly as a fuel or may be used for the production of a hydrogen containing gas by partial combustion with oxygen. In some instances it may be desirable to supply at least a portion of the hydrogen necessary for the process by partial combustion of the unconverted liquid oil. Overhead from bottoms separator 45 is removed through line 49.

Overhead from tower 17 comprising a mixture of hydrogen and vaporous hydrocarbons is withdrawn through line 31 and is cooled to a temperature of about 820–840° F. by the addition of a portion of condensed product from line 50. The cooled mixture is then subjected to additional cooling to a temperature below 800° F., preferably 700–750° F. in heat exchanger 52 where it is subjected to indirect heat exchange with recycle hydrogen after which the mixture is split into two substantially equal streams, one stream being introduced into hydrogenation reactor 54 through line 53 and the other stream being introduced into hydrogenation reactor 56 through line 55. Alternatively or additionally, the feed to reactors 54 and 56 may be subjected to liquid quench introduced into lines 53 and 55 through lines 57 and 58.

The feed inlets for reactors 54 and 56, which are operated in parallel, extend into a free space at the top of each reactor. The end of each inlet is closed but the sides are slotted to assist in the distribution of the feed mixture. Below each feed inlet there is maintained a fixed bed of hydrogenation catalyst, such as cobalt molybdate on alumina, covered by a stainless screen of fine mesh, through which, projecting into the catalyst bed to assist further in the distribution of the feed mixture, are baskets of stainless steel. The space velocity through the catalyst bed of each reactor preferably ranges from 1–4 volumes of normally liquid feed per volume of catalyst per hour, although space velocities of from 0.4–10 may be used. In hydrogenation reactors 54 and 56 the sulfur and nitrogen present in the hydrocarbons are converted respectively to hydrogen sulfide and ammonia and unsaturated gum-forming constituents are hydrogenated to stable compounds.

Effluent from hydrogenation reactor 54 passes through line 60, heat exchanger 61 and lines 62 and 63 to high pressure separator 69. Effluent from hydrogenation reactor 56 passes through line 64, heat exchanger 65, and lines 66 and 63 to high pressure separator 69. High pressure separator 69 although depicted as one vessel actually contains two chambers, the lower chamber acting as a separating chamber and the upper chamber as an amine scrubber. However for convenience the vessel is referred to simply as a high pressure separator. Reactor effluent is introduced into the lower chamber of high pressure separator through line 63. In the lower chamber, which is maintained at a temperature between about 110 and 120° F. and a pressure substantially that of reactors 54 and 56 except for the slight pressure drop incurred in the system, a separation is made between liquid and vaporous material. The vaporous material comprising hydrogen,

hydrogen sulfide and light hydrocarbon gases then passes upwardly through the upper chamber of high pressure separator 69 where scrubbing with an amine solution effectively removes the hydrogen sulfide. A hydrogen-rich gas essentially free from hydrogen sulfide and containing from 60 to 95 percent hydrogen is removed from high pressure separator 69 through line 67. To prevent the build-up of gases such as CH<sub>4</sub> or N<sub>2</sub> a bleed stream is withdrawn through line 80.

A portion of this hydrogen-rich gas is recycled through heat exchanger 52, lines 82 and 79 and is sent to heaters 13 and 27 through lines 21 and 19 respectively. A separate portion of the hydrogen-rich gas is withdrawn from line 67 through line 72 and is then split into two streams, one stream passing through line 75, heat exchanger 61 and lines 76 and 77 to be combined with recycle hydrogen from line 82. The other stream passes through line 83, heat exchanger 65, lines 74 and 77 to be combined with recycle hydrogen from line 82. Advantageously, the flow of hydrogen-rich gas through heat exchangers 65 and 61 is metered and the temperature of the gas before and after the heat exchangers is recorded. From this information the extent of the rate of flow in each of reactors 54 and 56 can be determined and if necessary the flow through reactors 54 and 56 can be equalized by means of control valves (not shown) in lines 64 and 60, or the reaction can be controlled by regulating the temperature of the feed to reactors 54 and 56.

The liquid product is withdrawn from high pressure separator 69 through line 50 and a portion, sufficient to cool the overhead from tower 17 about 30° F., is introduced into line 31. If necessary, sufficient product may also be sent through lines 57 and 58 to cool the feed to reactors 54 and 56 to a temperature below 800° F. The balance of the product liquid is sent to low pressure separator 85 through line 86. From low pressure separator 85 which is operated at a temperature of about 110° F. and a pressure of about 450 p.s.i.g. uncondensed gases are withdrawn through line 87 and combined with the bleed stream in line 80. Product liquid from low pressure separator is removed and sent to H<sub>2</sub>S stripper 90 through line 89. Steam introduced through line 91 expedites the removal of dissolved H<sub>2</sub>S from the hydrocarbons and the H<sub>2</sub>S containing stream is removed overhead through line 92. Liquid from H<sub>2</sub>S stripper 90 is sent through line 94 to product splitter 95 which may be a flash tower from which naphtha is removed overhead through line 96 and the balance of the product through line 97 or as a distillation column from which naphtha, kerosene and middle distillates are removed through lines 96, 98 and 97 respectively.

Make-up hydrogen may be introduced through line 63 into the recycle gas stream in line 67. When the hydrogen concentration of the make-up hydrogen is higher than the hydrogen concentration of the overhead from high pressure separator 69, this manner of introducing the make-up hydrogen is satisfactory. However, when the hydrogen concentration of the make-up hydrogen due, for example, to the presence of H<sub>2</sub>S, SO<sub>2</sub>, NH<sub>3</sub>, CO or CO<sub>2</sub>, is lower than the hydrogen concentration of the overhead from high pressure separator 69, the make-up hydrogen is advantageously introduced into the system through line 71. Introduced into the system through line 71, the make-up hydrogen passes with the reactor effluent into high pressure separator 69 and this procedure results in a recycle gas having a higher hydrogen concentration than would be the case if the make-up hydrogen were introduced through line 68.

Reference is now made to FIG. 3 which shows various modifications of the flow scheme of FIG. 1. Effluent from heater 13 flows through line 15 and may be introduced tangentially into the upper section of tower 17 which section serves as a disengaging zone to separate gasiform materials comprising vaporous hydrocarbons and hydro-

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gen from the liquid oil. The gasiform materials are removed overhead through line 31 and the disengaged liquid flows downwardly into the intermediate section of tower 17 where it is countercurrently contacted with an upwardly flowing stream of hot hydrogen introduced through line 29. The upwardly flowing hydrogen together with vaporous hydrocarbons removed from the hydrocarbon liquid and also vaporous hydrocarbons formed in the intermediate section of tower 17 may be withdrawn below baffle 37 as a side stream through line 32 and combined with the overhead from tower 17 in line 31.

Unvaporized liquid collects in the lower section of tower 17. To agitate the unvaporized hydrocarbon liquid and to facilitate further handling thereof, hydrogen or a light hydrocarbon gas such as methane may be introduced into the liquid upstream of valve 40 as for example into boot 34 through line 38.

As an alternative to quenching overhead in line 31 or in addition thereto, liquid quench may be introduced through line 50 into line 32. It is also advantageous in some instances, as for example, when heater 13 is operated under severe conditions, to introduce liquid quench into the heater effluent in line 15 through line 51.

Any hydrocarbon liquid may be converted by the process of the present invention. However, the process of the present invention has particular application in the treatment of hydrocarbon liquids containing residual components, metals and other tar- and ash-forming constituents, particularly hydrocarbon liquids having Conradson carbon values of at least about 1% by weight or having metal contents of at least 5 p.p.m. Examples of charge stocks to which the process of the invention may be applied successfully are crude oils and heavy fractions of crude oils such as Santa Maria crude, San Ardo crude, Arabian crude, reduced or topped crude, vacuum residuum and mixtures thereof and the like. Other materials which may be advantageously treated are coal oil, pitches, tars, gilsonite, shale oil and tar sand oil.

The process of the present invention is characterized by the circulation of large volumes of hydrogen far in excess of the stoichiometric hydrogen requirements of the conversion. The hydrogen employed in the system may be substantially pure, e.g., 90-97% pure or may be dilute hydrogen such as a gas mixture containing as little as 40% hydrogen by volume obtained, for example, by the partial combustion of carbonaceous fuels. Suitable sources of hydrogen are catalytic reformer hydrogen, electrolytic hydrogen or synthesis gas which may be used as produced by the partial combustion of a carbonaceous fuel or after being subjected to a water gas shift reaction and CO<sub>2</sub> removal to produce hydrogen of about 95% purity. The term "hydrogen" as used in the present specification and appended claims includes not only pure hydrogen but also includes dilute hydrogen. Preferably, the recycle gas contains at least 60 vol. percent hydrogen.

As pointed out above, hydrogen is passed through the system in amounts far in excess of the amount of hydrogen consumed in the process. Total hydrogen rates ranging from 10,000 up to 100,000 standard cubic feet per barrel of charge stock, preferably 13,000 to 80,000 cubic feet of hydrogen per barrel of feed, are used. From 10 to 60% of the hydrogen is introduced into the heating coil with the feed and at least 20% of the hydrogen but not less than 5,000 s.c.f./bbl. is introduced at the bottom of the contacting tower. Total overall hydrogen consumption varies from about 500 to 1,500 s.c.f./bbl. with the consumption of hydrogen ranging from about 25% to 40% in the heating coil, 10% to 20% in the contacting tower and 40% to 65% in the catalytic unit.

To replace the hydrogen consumed in the process make-up hydrogen, in an amount substantially equal to that consumed, is introduced into the system. The composition of the make-up hydrogen determines to a large extent at which point in the system it is introduced.

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When the concentration of hydrogen in the make-up hydrogen is lower than the hydrogen concentration of the overhead from the high pressure separator the make-up hydrogen is advantageously introduced into the system before the high pressure separator, and when the hydrogen concentration of the make-up hydrogen is higher than the hydrogen concentration of the overhead from the high pressure separator the make-up hydrogen may then be introduced into the recycle gas stream. This general rule of determining the point of introduction of the make-up hydrogen should be followed, particularly when the impurities in the make-up hydrogen are H<sub>2</sub>S, SO<sub>2</sub>, NH<sub>3</sub>, CO, CO<sub>2</sub> or methane or other light hydrocarbons. However, when the bulk of the impurities present in the make-up hydrogen is methane or other light hydrocarbons, the make-up hydrogen may then be introduced into the recycle gas stream and advantageously is introduced into the system to flow directly with the separately heated hydrogen into the lower section of the contacting tower.

The mixture of hydrogen and oil is introduced into a heater containing a tubular coil which preferably is constructed of tubing composed of a steel alloy containing minor amounts of chromium, molybdenum and nickel.

For effective first stage conversion of the charge stock the reactants must pass through the heating coil under conditions of violently turbulent flow. The hydrocarbon feed rate, hydrogen rate, reaction coil diameter and operating conditions of temperature and pressure all tend to affect the velocity of flow and the turbulence. It has been found convenient to express turbulence in terms of the ratio of the average apparent viscosity of the flowing stream,  $\bar{\epsilon}m$ , to the molecular or kinematic viscosity  $\nu$ , viz.

$$\frac{\bar{\epsilon}m}{\nu}$$

Hereinafter, we shall refer to this ratio,

$$\frac{\bar{\epsilon}m}{\nu}$$

as turbulence level. The apparent viscosity of the flowing stream,  $\epsilon m$ , equals the sum of the eddy viscosity,  $\epsilon m$ , and the kinematic viscosity  $\nu$  which may be shown in the expression  $\epsilon m = \epsilon m + \nu$ . Under conditions of turbulence,  $\epsilon m$  has a finite value and it is apparent that if the magnitude of the apparent viscosity exceeds the kinematic viscosity at the point in question, the ratio of

$$\frac{\epsilon m}{\nu}$$

exceeds unity. For a given turbulent system, it follows that the average value of the ratio, as expressed by

$$\frac{\bar{\epsilon}m}{\nu}$$

exceeds unity. The average apparent viscosity,  $\bar{\epsilon}m$  as employed herein is defined by the equation

$$\bar{\epsilon}m = \frac{1}{r_o} \int_0^{r_o} \epsilon m dr$$

where  $r_o$  is the radius of the conduit. By substitution and integration, employing the parameters described by Corcoran et al., Industrial and Engineering Chemistry, 44, 410 (1952), this expression

$$\bar{\epsilon}m = \frac{1}{r_o} \int_0^{r_o} \epsilon m dr$$

may be rewritten

$$\bar{\epsilon}m = \frac{r_o}{15} \sqrt{\frac{r_o g}{2\sigma}} \frac{dp}{dx}$$

The latter equation is in terms which may be readily determined for a given system,

$$\frac{dp}{dx}$$

being the pressure drop per unit of conduit length. In the process of this invention, turbulence levels of 25 and higher may be employed but turbulence levels of 50 to 1,000 are preferable. At turbulence levels below 25, a heavy tar-like material is formed at the expense of the desired products. This tar-like material can cause fouling and plugging of the apparatus requiring frequent shut-downs.

In the foregoing paragraph, the various symbols used in the formulas are defined as follows:

$d$ =differential

$g$ =acceleration of gravity, feet per second<sup>2</sup>

$p$ =pressure, pounds per square foot

$r$ =radial distance from center of conduit, feet

$r_0$ =radius of conduit, feet

$x$ =distance, feet

$\epsilon m$ =eddy viscosity, square feet per second

$\bar{\epsilon m}$ =apparent viscosity, square feet per second

$\bar{\epsilon m}$ =average apparent viscosity, square feet per second

$\nu$ =kinematic viscosity, square feet per second

$\sigma$ =specific weight, pounds per cubic foot

As the mixture of hydrogen and oil passes through the coil and is heated the lighter and intermediate boiling range materials present in the feed become vaporized so that, when reaction temperature is reached the mixture is in the form of a mist of fine droplets suspended in a gaseous phase comprising hydrogen and vaporous hydrocarbons. The amount of hydrocarbon vapors present in the reaction mixture depends upon temperature, pressure and the amount of low boiling range and intermediate boiling range material present in the feed but in any event, the amount of hydrocarbon vapor is small relative to the volume of hydrogen present and has little effect on the formation of the reaction mixture. In other words, under the conditions present, the reaction mixture, when heated to reaction temperature, will be in the form of a mist of liquid hydrocarbon droplets suspended in a gaseous phase whether or not the feed contains a relatively large or a relatively small amount of low boiling and intermediate boiling range materials.

Without intending to be bound thereby, we present the following theory. Due to the large volume of hydrogen present, the high partial pressure of the hydrogen and the fineness of the oil droplets because of the violently turbulent condition in the coil, the hydrogen diffuses into and saturates the oil droplets so that when the high boiling hydrocarbons of the droplets are split into fragments, there is sufficient hydrogen present throughout the system including the liquid phase to saturate these fragments as they are formed and thereby prevent further splitting of the fragments into lighter boiling fractions or fixed gases or prevent the unsaturated fragments from inter-reacting to form heavy tars.

Effluent from the heating coil is introduced into the upper portion of the contacting tower where a separation is made between the gasiform material and the liquid material. The upper portion of the tower is a free space of enlarged cross section relative to the cross section of the heating coil and due to the reduction in velocity of the heater effluent and the reduced turbulence, the liquid settles from the gasiform material. While it may be possible to use mechanical devices to assist in the separation of the liquid from the gases such as, for example, a cyclone type separator or a contact material to which the liquid can adhere, it has been found that operation of the tower with a free space in the upper section is satisfactory and there is substantially no entrainment of liquid with the gaseous materials. A separately heated stream of hot hydrogen, amounting to at least

about 20% of the hydrogen passed through the system but not less than 5,000 s.c.f./bbl. is introduced into the contacting tower in the lower section thereof.

The disengaged liquid flows downwardly through the intermediate section of the tower which is so arranged as to bring the descending liquid into intimate contact with the ascending stream of hot hydrogen. Preferably, the intermediate section of the tower is equipped with baffles of the "disk and donut" type although in some instances an inert filling material such as ceramic balls or Raschig rings or gravel may be used satisfactorily. The upwardly-flowing hot hydrogen serves to remove dissolved or entrained vaporous hydrocarbons from the descending liquid stream. In addition, some cracking of the liquid hydrocarbons in the tower also takes place probably due at least in part to the prolonged residence time of the liquid hydrocarbons at high temperatures. The cracked fragments are also hydrogenated as is evidenced by an increase in the temperature of the intermediate section of the tower at points spaced above the hydrogen inlet. The hydrogenated fragments which are lower boiling than the liquid are vaporized under the prevailing conditions and, together with the other vaporous hydrocarbons removed from the liquid, are swept upwardly through the tower with the ascending hydrogen stream to further increase the yield of middle distillates.

One of the unique features of the process of the present invention is the operation of the contacting tower at pressures considerably in excess of the pseudo-critical pressure of the charge oil. Ordinarily, in any distillation or fractionation, the operating pressure is below the pseudo-critical pressure of the charge stock. However, in the practice of the present invention the operating pressure of the contacting tower is considerably above the pseudo-critical pressure of the charge stock yet in the tower there is effected a separation from the unconverted liquid portion of the charge not only of the middle distillates produced in the process but also the middle distillate and lighter materials present in the charge stock. The pseudo-critical pressures referred to herein are determined by the method of Smith and Watson described at page 1408 of Industrial and Engineering Chemistry, vol. 29 (1937).

The unconverted liquid which contains substantially all of the metals and ash-forming constituents present in the charge is collected in the lower portion of the tower below the point of introduction of the hot hydrogen. Depending on the quality of the charge stock, the volume of the tower bottoms will range from about 5-25% of the charge. For example, when Arabian crude is charged to the system the volume of the tower bottoms will be about 5-10% of the charge whereas San Ardo crude or the like will yield about 10-25% bottoms. To reduce the viscosity of the bottoms to facilitate further handling, and to cool the bottoms to a temperature of about 500° F., a light oil such as, for example, a light cycle gas oil, is added as a cutter oil to the withdrawn bottoms and the mixture may then be contacted with steam to remove trace amounts of dissolved gases such as hydrogen, nitrogen and methane. The stripped bottoms may then be subjected to further treatment or may be used as a distillate fuel or may be used to produce at least a portion of the hydrogen required for the process by partial combustion with oxygen in a manner such as disclosed in U.S. Patent No. 2,701,756 to Eastman et al.

Overhead from the contacting tower which comprises hydrogen and vaporous hydrocarbons from the heating coil and hydrogen and vaporous hydrocarbons from the tower is cooled from a temperature of 840-900° F. to a maximum temperature of 800° F., preferably 700-750° F. prior to being subjected to catalytic treatment. The cooling may be effected in any suitable manner as by direct or indirect heat exchange or both. It has been

found advantageous to cool the overhead partially by the direct addition thereto of a portion of cooled liquid product and to complete the cooling to the desired temperature by indirect heat exchange with recycle hydrogen. However, it will be obvious to those skilled in the art that all of the cooling may be effected by one heat exchange means or the other and that various streams from within the process or from an external source may be used as exchange media. Obviously, however, a stream which would introduce undesirable materials such as metal and ash-forming constituents or heavy residual constituents into the overhead would be unsatisfactory as a direct heat exchange medium.

As the catalytic treatment is carried out at a pressure generally in excess of 1,000 p.s.i.g., it is advisable in larger plants, to use two catalytic chambers as shown in accompanying FIG. 1. In smaller plants, one catalytic chamber is generally satisfactory.

The cooled mixture is contacted with a hydrogenation catalyst. Suitable catalysts comprise the oxides and/or sulfides of metals such as cobalt, molybdenum, nickel, tungsten, chromium, iron, manganese, vanadium and mixtures thereof. The catalytic materials may be used alone or may be deposited on or mixed with a support such as alumina, magnesia, silica, zinc oxide or the like. Particularly suitable catalysts are nickel tungsten sulfide, molybdenum oxide on alumina, a mixture of cobalt oxide and molybdenum oxide generally referred to as cobalt molybdate on alumina, molybdenum oxide and nickel oxide on alumina, molybdenum oxide, nickel oxide and cobalt oxide on alumina, nickel sulfide on alumina, molybdenum sulfide, cobalt sulfide and nickel sulfide on alumina. Although these catalysts are generally considered hydrogenation catalysts, a considerable amount of conversion of the heavier hydrocarbons present into lighter boiling materials takes place in the catalyst chamber, probably due at least in part to the treatment to which the feedstock has been subjected prior to its introduction into the catalyst chamber.

Hydrogen rates in the catalytic treating zone are high. The total hydrogen supply to the system, comprising hydrogen introduced into the heating coil and the separately-heated hydrogen introduced into the lower section of the contacting tower, amounts to at least 10,000 cu. ft./bbl. of oil fed to the heating coil. Some of the hydrogen is consumed in the heating coil and some is consumed in the contacting tower. This hydrogen consumption prior to the introduction of the reactants into the catalyst chamber amounts to from about 200 to 800 cu. ft./bbl. of feed and accordingly does not amount to more than about 10% of the hydrogen supply. However, since the amount of bottoms withdrawn from the contacting tower is about 5-20 volume percent of the feedstock, the hydrogen rate in the catalytic treating zone is still of the order of at least about 10,000 cu. ft./bbl. of liquid hydrocarbon charge, an amount much higher than is used in conventional catalytic hydrogenation operations.

The process of the present invention is particularly advantageous in several respects. In the first place, the conversion of heavy oils into high yields of middle distillates boiling in the 400-700° F. range without the formation of tars and coke is much greater than is obtainable by the conventional atmospheric-vacuum distillation methods. The product middle distillates, because of their high hydrogen content, and low metal content are valuable as cracking feed stock.

Another advantageous feature of the present invention is the excellent temperature-viscosity relationship of the lube oil fraction of the product as evidenced by a viscosity index in the neighborhood of 100 without further treatment.

Another advantage is the high purity of the recycle hydrogen. Operation of the high pressure separator at

a pressure usually in excess of about 1,400 p.s.i.g. results in a recycle gas containing negligible amounts of condensable materials such as C<sub>3</sub>-C<sub>5</sub> hydrocarbons. Under ordinary circumstances, the high pressure separator overhead has a hydrogen concentration ranging from about 65 to about 95 volume percent hydrogen. A typical analysis of the overhead is as follows:

|                                      | Mol. percent |
|--------------------------------------|--------------|
| H <sub>2</sub> -----                 | 87.745       |
| CO -----                             | 0.060        |
| CO <sub>2</sub> -----                | 0.020        |
| N <sub>2</sub> -----                 | 1.115        |
| H <sub>2</sub> S -----               | 0.905        |
| CH <sub>4</sub> -----                | 8.150        |
| C <sub>2</sub> H <sub>6</sub> -----  | 1.160        |
| C <sub>3</sub> H <sub>8</sub> -----  | 0.585        |
| C <sub>4</sub> H <sub>10</sub> ----- | 0.260        |

Furthermore, the present process yields a product which is substantially free from sulfur, nitrogen and metals. The product is also stable and is essentially free from gum-forming constituents. Another advantage is the reduction over conventional apparatus in the amount of corrosion resistant equipment which must be used. In ordinary refining methods the crude oil or charge stock is fractionated into separate fractions, each of which is separately treated, thus requiring a multiplicity of corrosion resistant equipment such as fractionators, reactors and storage facilities. In the present process the need for corrosion resistant equipment is reduced to a minimum.

Another advantage of the process is the effective use of a nominal hydrogenation catalyst not only for hydrogenation but also for the conversion of heavier hydrocarbons into lighter hydrocarbons.

Still another advantage of the present process is the long life of the hydrogenation catalyst in view of the heavy material fed thereto. In conventional hydrogenation processes where a substantial portion of the feed to the catalyst boils in the middle distillate range and higher, the catalyst life is relatively short because of the deposition of large amounts of coke and carbon on the catalyst. In the present process the catalyst life is much longer than in conventional processes currently being used in the industry, apparently due at least in part, to the high hydrogen recirculation rates.

Another advantage of the process is that all of the reactions are conducted at substantially the same pressure, thereby eliminating the need for intermediate compressors. It should be understood of course, that the reactants incur a slight pressure drop in the range of about 150-250 p.s.i. as they pass through the heating coil, the contacting tower and the catalyst chamber.

The following example is given for illustrative purposes only and should not be construed as limiting the invention in any manner.

#### EXAMPLE

The feedstocks used in this example are heavy oils having the following characteristics:

| Run No. ....                                | 1     | 2     | 3     |
|---------------------------------------------|-------|-------|-------|
| Gravity, °API .....                         | 14.7  | 15.3  | 32.6  |
| Viscosity, SSF/122 .....                    | 238.3 | 198.5 | 145.7 |
| Conradson Carbon Residue, wt. percent ..... | 6.4   | 6.5   | 3.66  |
| Sulfur, wt. percent .....                   | 2.01  | 1.82  | 1.88  |
| Nitrogen, wt. percent .....                 | 0.7   | 0.7   | 0.06  |
| Distillation Range, vol. percent recovered: |       |       |       |
| IBP-400° F .....                            | 1.3   | 1.3   | 29.7  |
| 400-500° F .....                            | 7.7   | 7.7   | 12.0  |
| 500-700° F .....                            | 30.3  | 30.3  | 29.3  |
| 700° F. + .....                             | 60.7  | 60.7  | 29.0  |
| Metals, p.p.m.:                             |       |       |       |
| Vanadium .....                              | 40    | 40    | 5.7   |
| Nickel .....                                | 60    | 60    | 2.8   |
| Pseudo critical pressure, p.s.i.a. ....     | 145   | 145   | 305   |

Operating conditions and other data are listed below:

| Run No.                                                            | 1      | 2      | 3      |
|--------------------------------------------------------------------|--------|--------|--------|
| Pressure, p.s.i.g.:                                                |        |        |        |
| Hydrogen heater inlet                                              | 1,600  | 1,567  | 1,558  |
| Oil-hydrogen heater inlet                                          | 1,562  | 1,642  | 1,582  |
| Contacting tower outlet                                            | 1,484  | 1,495  | 1,491  |
| Catalyst chamber outlet                                            | 1,433  |        | 1,425  |
| High pressure separator                                            | 1,423  | 1,444  | 1,418  |
| Turbulence level in oil-hydrogen heater                            | 180    | 195    | 210    |
| Flows, s.c.f. per bbl. of oil feed:                                |        |        |        |
| Hydrogen to heating coil                                           | 18,400 | 11,300 | 8,600  |
| Hydrogen to contacting tower                                       | 62,700 | 40,600 | 28,100 |
| Hydrogen concentration, vol. percent                               | 87.75  | 92.56  | 91.86  |
| Temperature, ° F.:                                                 |        |        |        |
| Oil-hydrogen heater                                                | 826    | 831    | 801    |
| Oil inlet to tower                                                 | 770    |        | 747    |
| Hydrogen inlet to tower                                            | 813    | 827    | 815    |
| Tower 3" above hydrogen inlet                                      | 826    | 830    | 850    |
| Tower overhead outlet                                              | 790    | 814    | 811    |
| Catalyst <sup>2</sup> chamber inlet                                | 789    | (4)    | 793    |
| Catalyst chamber outlet                                            | 733    | (4)    | 738    |
| Space velocity in catalyst chamber v. oil/v. cat./hr. <sup>3</sup> | 0.5    |        | 0.5    |
| Product liquid:                                                    |        |        |        |
| Yield, vol. percent                                                | 92.2   | 82.3   | 90.67  |
| °API Gravity                                                       | 30.0   | 22.5   | 44.4   |
| Viscosity SSU at 100° F                                            | 44.6   | 80.8   | 33.3   |
| Sulfur, wt. percent                                                | 0.02   | 1.73   | 0.02   |
| Nitrogen, wt. percent                                              | 0.07   | 0.52   | 0.02   |
| Carbon residue, wt. percent                                        | 0.01   | 1.34   | 0.00   |
| Vanadium, p.p.m.                                                   | <1.0   | <10    | 0.1    |
| Nickel, p.p.m.                                                     | 0.1    | 4.8    | 0.1    |
| Distillation Range, vol. percent recovered:                        |        |        |        |
| IBP-400° F                                                         | 14.0   | 7.7    | 36.7   |
| 400-500° F                                                         | 17.3   | 13.7   | 16.3   |
| 500-700° F                                                         | 44.0   | 30.0   | 33.3   |
| 700° F <sup>2</sup>                                                | 24.7   | 48.6   | 13.7   |
| Tower Bottoms:                                                     |        |        |        |
| Yield, vol. percent                                                | 18.40  | 20.96  | 8.6    |
| °API Gravity                                                       | 5.7    | 4.2    | 6.3    |
| Vanadium, p.p.m.                                                   | 314    | 224    | 85     |
| Nickel, p.p.m.                                                     | 255    | 122    | 15     |
| Sulfur, wt. percent                                                | 2.0    | 1.91   | 4.0    |
| Carbon residue, wt. percent                                        | 11.6   | 21.9   | 21.6   |
| Apparent Hydrogen Consumption, s.c.f./bbl.                         | 983    | 234    | 997    |

<sup>1</sup> SSU/122.

<sup>2</sup> Cobalt molybdate on alumina.

<sup>3</sup> Based on charge to oil-hydrogen heater.

<sup>4</sup> No catalytic treatment.

<sup>5</sup> 122° F.

Distillation data on the feedstocks for run 1, which is substantially identical with that of run 2, and for the product liquids of runs 1 and 2 are plotted in the accompanying FIGURE 2. The curves show a feedstock middle distillate (400-700° F.) content of 24.5 barrels per 100 barrels. Run 2 shows that for each 100 barrels of charge fed to the heating coil and contacting tower, there is obtained 32.9 barrels of middle distillate. However, in run 1 in which the heating coil, contacting tower and catalytic unit are used 100 barrels of feed yield 56.2 barrels of middle distillate. It will also be noted from the curve for run 2, that there is a greater conversion to middle distillate in the catalytic hydrogenation zone than in either of the other reaction zones.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

This application is a continuation-in-part of our copending application S.N. 765,318, filed October 6, 1958 now abandoned, and is also a continuation-in-part of our copending application S.N. 740,138, filed June 5, 1958 now U.S. Patent No. 2,989,461, which, in turn, is a continuation-in-part of our application S.N. 577,027, filed April 9, 1956, and now abandoned.

We claim:

1. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g.,

separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and recovering a normally liquid hydroconversion product from the catalytic treating zone effluent.

2. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt, which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, countercurrently contacting said liquid portion in a non-catalytic contacting zone with a hydrocarbon stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and recovering a normally liquid hydroconversion product from the catalytic treating zone effluent.

3. The process of claim 2 in which the contacting zone is maintained at a pressure above the pseudo critical pressure of the hydrocarbon oil feed stock.

4. A process for the hydroconversion of a hydrocarbon oil selected from the group consisting of crude oil, reduced crude oil, deasphalted residuum, shale oil, tar sand oil and mixtures thereof which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about

800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of a normally liquid feed per volume of catalyst per hour and recovering a normally liquid hydroconversion product from the catalytic treating zone effluent.

5. A process for the hydroconversion of a hydrocarbon oil having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen, said mixture containing between 7,000 and 30,000 cubic feet of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, countercurrently contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to between 8,000 and 60,000 cu. ft. per barrel of oil charged to said reaction zone to produce additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact, in a catalytic treating zone, with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and recovering a normally liquid hydroconversion product from the catalytic treating zone effluent.

6. A process for the conversion of a sulfur and metal containing hydrocarbon oil having a Conradson carbon residue of at least 1.0% by wt. into a hydrocarbon liquid fraction of reduced sulfur, metal and carbon residue content which comprises passing an intimate mixture of said oil and hydrogen, said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil, as a confined stream through an elongated reaction zone at a temperature between about 700 and 900° F., a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g. and at a turbulence level of at least 25, separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with

a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and recovering a normally liquid hydroconversion product from the catalytic treating zone effluent.

7. The process of claim 6 in which the pressure in the reaction zone, the contacting zone and the catalytic treating zone is substantially the same.

8. The process of claim 7 in which the pressure in the reaction zone is between about 1,400 and 2,000 p.s.i.g.

9. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour, separating the effluent from the catalytic treating zone into a gaseous fraction rich in hydrogen and a normally liquid fraction and recycling a portion of said gas rich in hydrogen to said reaction zone.

10. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour, separating the effluent from the catalytic treat-

ing zone into a gas rich in hydrogen and a normally liquid product passing a portion of the gas rich in hydrogen in indirect heat exchange with said combined stream and passing a separate portion of said gas rich in hydrogen in indirect heat exchange with the effluent from said catalytic treating zone.

11. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour, separating the effluent from the catalytic treating zone into a gas rich in hydrogen and a normally liquid product and introducing a portion of the normally liquid product into said combined stream to partially cool said combined stream.

12. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour, separating the effluent from the catalytic treating zone into a gas rich in hydrogen and a normally liquid product and introducing a portion of the normally liquid product into said reaction zone effluent to

partially cool said reaction zone effluent prior to separating said reaction zone effluent into a gasiform portion and a liquid portion.

13. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst comprising molybdenum oxide at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and recovering a normally liquid hydroconversion product from the catalytic treating zone effluent.

14. A process for the hydroconversion of a hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. which comprises passing an intimate mixture of said oil and hydrogen said mixture containing at least 5,000 standard cu. ft. of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply but not less than 5,000 cu. ft. per barrel, the total hydrogen supply amounting to between 10,000 and 100,000 standard cu. ft. per barrel, of oil charged to the reaction zone, thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a hydrogenation catalyst comprising molybdenum oxide and the oxide of a group VIII metal at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and recovering a normally liquid hydroconversion product from the catalytic treating zone effluent.

15. The process of claim 14 in which the group VIII metal is cobalt.

16. The process of claim 14 in which the group VIII metal is nickel.

17. A process for the conversion of a sulfur and metal

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containing hydrocarbon oil feedstock having a Conradson carbon residue of at least 1.0% by wt. into a liquid product of reduced sulfur, metal and carbon residue content which comprises passing an intimate mixture of said oil and hydrogen, said mixture containing between 7,000 and 30,000 cubic feet of hydrogen per barrel of oil, as a confined stream through an elongated reaction zone at a temperature between about 700 and 900° F., a pressure between 1,400 and 2,000 p.s.i.g., and a turbulence level of at least 25, separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, countercurrently contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to between 8,000 and 60,000 cu. ft. per barrel of oil charged to said reaction zone to produce additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last-mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, separately removing from said contacting zone a residue containing substantially all of the metals present in said hydrocarbon oil feedstock passing the combined hydrogen and vaporous hydrocarbons and gasiform portion into contact with a hydrogenation catalyst comprising the oxides of molybdenum and a group VIII metal at a temperature between about 600 and 800° F. and a liquid hourly space velocity of from about 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and separating the effluent from the catalytic treating zone into a gas rich in hydrogen and a liquid product of reduced sulfur, metal and carbon residue content.

18. Apparatus suitable for the conversion of hydrocarbon liquids comprising in combination a pressure resistant contacting tower having top and bottom outlets, said tower comprising an upper disengaging section, an intermediate contacting section and a lower liquid collecting section, a first inlet leading into said upper disengaging section and a second inlet leading into said contacting section, a first heater having an inlet and an outlet, a line connecting said first heater outlet with said first inlet, means for passing a reactant stream under conditions of highly turbulent flow through said first heater, a second heater having an inlet and an outlet, said second heater outlet being connected to said second inlet, a catalyst chamber, an inlet leading into said catalyst chamber, a line connecting said catalyst chamber inlet with said top outlet, an outlet from said catalyst chamber opposed to the catalyst chamber inlet, a high pressure separator having an inlet, an upper outlet and a lower outlet, said high pressure separator inlet being connected to the catalyst chamber outlet and a line connecting said upper outlet to said first heater inlet.

19. The apparatus of claim 18 including a line connecting said lower outlet with said line connecting the catalyst chamber inlet with the top outlet.

20. The apparatus of claim 18 including a line connecting said lower outlet with the line connecting said first heater outlet with said first inlet.

21. Apparatus suitable for the conversion of hydrocarbon liquids comprising in combination a pressure resistant contacting tower having top and bottom outlets, said tower comprising an upper disengaging section, an intermediate contacting section having baffles disposed therein and a lower liquid collecting section, a first inlet leading into said upper disengaging section and a second inlet leading into said contacting section at a point spaced below said baffles, a first heater having an inlet and an outlet, a line connecting said first heater outlet with said first inlet, means for passing a reactant stream under conditions of highly turbulent flow through said first

heater, a second heater having an inlet and an outlet, said second heater outlet being connected to said second inlet, a catalyst chamber, an inlet leading into said catalyst chamber, a line connecting said catalyst chamber inlet with said top outlet, an outlet from said catalyst chamber opposed to the catalyst chamber inlet, a high pressure separator having an inlet, an upper outlet and a lower outlet, said high pressure separator inlet being connected to the catalyst chamber outlet and a line connecting said upper outlet to said first and second heater inlets.

22. A process for the production of a hydrocarbon liquid of reduced sulfur, metal and carbon residue content which comprises passing an intimate mixture of hydrogen and a sulfur and metal containing hydrocarbon oil having a Conradson carbon residue of at least 1.0% by wt., said mixture containing at least 5,000 standard cubic feet of hydrogen per bbl. of oil as a confined stream through an elongated reaction zone, at a temperature between about 700 and 900° F., a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g. under conditions of highly turbulent flow, separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, countercurrently contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to at least 20% by volume of the total hydrogen supply, but not less than 5,000 cubic feet per bbl., the total hydrogen supply amounting to between 10,000 and 100,000 standard cubic feet per bbl., of oil charged to the reaction zone to produce additional hydrocarbon vapors in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, separating the resulting combined stream into a plurality of divided streams, passing each of said divided streams into contact, in separate catalytic treating zones, with a hydrogenation catalyst at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour combining the catalytically treated divided streams and separating from the so-produced combined stream a gas rich in hydrogen and a hydrocarbon liquid product of reduced sulfur, metal and carbon residue content.

23. A process for the production of a hydrocarbon liquid of reduced sulfur, metal and carbon residue content which comprises passing an intimate mixture of hydrogen and a sulfur and metal containing hydrocarbon oil having a Conradson carbon residue of at least 1.0% by wt., said mixture containing between 7,000 and 30,000 cubic feet of hydrogen per bbl. of oil, as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, countercurrently contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to between 8,000 and 60,000 cubic feet per bbl. of oil charged to said reaction zone thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last-mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, separating the combined stream into substantially equal portions, passing

each of said substantially equal portions into contact, in separate catalytic treating zones, with a catalyst comprising a compound of molybdenum and a compound of a group VIII metal at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 volumes of normally liquid feed per volume of catalyst per hour and recovering a hydrocarbon liquid of reduced sulfur, metal and carbon residue content from the effluent from the catalytic treating zones.

24. A process for the production of a hydrocarbon liquid of reduced sulfur, metal and carbon residue content which comprises passing an intimate mixture of hydrogen and a sulfur and metal containing hydrocarbon oil having a Conradson carbon residue of at least 1.0% by wt. said mixture containing between 7,000 and 30,000 cubic feet of hydrogen per barrel of oil as a confined stream through an elongated reaction zone under conditions of turbulent flow at a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g. separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, counter-currently contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to between 8,000 and 60,000 cu. ft./bbl. of oil charged to said reaction zone whereby producing additional vaporous hydrocarbons in said contacting zone, withdrawing from said contacting zone a hydrocarbon residue containing substantially all of the metal and carbon residue content of the hydrocarbon oil feed, separately removing from said contacting zone unreacted hydrogen and vaporous hydrocarbons, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, separating the combined stream into a plurality of divided streams, passing each of said divided streams into contact in separate catalytic treating zones with a catalyst comprising an oxide of molybdenum and an oxide of a group VIII metal at a temperature between 600 and 800° F. and a liquid hourly space velocity, in each of said catalytic treating zones, between 0.4 and 10 vols. of normally liquid feed per volume of catalyst per hour, recovering from the effluent from said catalytic treating zones a gas rich in hydrogen and a product liquid of reduced sulfur, metal and carbon residue content, recycling a portion of said gas rich in hydrogen to said reaction zone, passing a portion of the recycle stream in indirect heat exchange relationship with said combined stream, passing a separate portion of the recycle stream in indirect heat exchange relationship with effluent from the catalytic treating zones and partially cooling said combined stream by the addition thereto of a portion of said product liquid.

25. A process for the production of a hydrocarbon liquid of reduced sulfur, metal and carbon residue content which comprises passing an intimate mixture of hydrogen and a sulfur and metal containing hydrocarbon oil having a Conradson carbon residue of at least 1.0% by wt., said mixture containing between 7,000 and 30,000 cu. ft. of hydrogen per bbl. of oil as a confined stream through an elongated reaction zone at a turbulence level between 50 and 1,000, a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, counter-currently contacting said liquid portion in a non-catalytic contacting zone with a hydrogen stream separately heated to a temperature between about 800 and

900° F. and amounting to between 8,000 and 60,000 cu. ft. per bbl. of oil charged to said reaction zone thereby producing additional vaporous hydrocarbons in said contacting zone, withdrawing from said contacting zone a hydrocarbon residue containing substantially all of the metal and carbon residue content of the hydrocarbon oil feed, separately removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, passing the combined stream into contact in a catalytic treating zone with a catalyst comprising the sulfides of molybdenum and a group VIII metal at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 vols. of normally liquid feed per vol. of catalyst per hour, passing the effluent from the catalytic treating zone into a high pressure separation zone, separating the effluent from the catalytic treating zone into a gas rich in hydrogen and a liquid product of reduced sulfur, metal and carbon residue content, scrubbing said gas at substantially the pressure of the high pressure separation zone with an amine solution and recycling a portion of said scrubbed gas rich in hydrogen to said reaction zone.

26. A process for the production of a hydrocarbon liquid of reduced sulfur, metal and carbon residue content which comprises passing an intimate mixture of hydrogen and a sulfur and metal containing hydrocarbon oil having a Conradson carbon residue of at least 1.0% by wt., said mixture containing between 7,000 and 30,000 cu. ft. of hydrogen per bbl. of oil as a confined stream through an elongated reaction zone at a turbulence level between 50 and 1,000, a temperature between about 700 and 900° F. and a pressure not less than 1,000 p.s.i.g. and not greater than about 5,000 p.s.i.g., passing the reaction zone effluent without any substantial reduction in pressure to a separation zone, separating the reaction zone effluent comprising hydrogen, vaporous hydrocarbons and liquid hydrocarbons into a gasiform portion comprising hydrogen and vaporous hydrocarbons and a liquid portion comprising unvaporized hydrocarbons, countercurrently contacting said liquid portion in a non-catalytic contacting zone at substantially the pressure of the reaction zone with a hydrogen stream separately heated to a temperature between about 800 and 900° F. and amounting to between 8,000 and 60,000 cu. ft. per bbl. of oil charged to said reaction zone thereby producing additional vaporous hydrocarbons in said contacting zone, removing unreacted hydrogen and vaporous hydrocarbons from the contacting zone, combining said last mentioned unreacted hydrogen and vaporous hydrocarbons with said gasiform portion, contacting the combined stream in a catalytic treating zone at substantially the pressure of the contacting zone with a catalyst comprising the oxides of molybdenum and a group VIII metal at a temperature between 600 and 800° F. and a liquid hourly space velocity of from 0.4 to 10 vols. of normally liquid feed per vol. of catalyst per hour and recovering from the catalytic treating zone effluent a product hydrocarbon liquid of reduced sulfur, metal and carbon residue content.

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